氏名	房　　少立
学位（専攻分野）	博士（理学）
学位記番号	総研大甲第１０３号
学位授与の日付	平成６年９月２０日
学位授与の要件	数物科学研究科　機能分子科学専攻 学位規則第４条第１項該当
学位論文題目	Nonlinear Optical Properties of Phthalocyanine Thin Films Grown by the Molecular-Beam-Epitaxy Method
論文審査委員	主査　教授　薬師久彌 教授　丸山有成 助教授　鹿野田一司 教授　北川禎三 助教授　大内幸雄（名古屋大学）

論文内容の要旨

Study on the electronic and photonic properties of organic molecular solids has recently been an important subject in the fields of both basic physical science and applied materials science. There are two important factors which determine the solid state properties of molecular solids. The first one is the characteristic nature of the constituting molecules. The second one is the intermolecular interaction which may strongly depend on the nature of moleculesa nd also the molecular assembly structure. Thus, controlling the structures of molecular assemblies results in control of the functional properties of the solids. Therefore, the theme of the present thesis is to fabricate highly-ordered, well-characterized ultrathin films of phthalocyanine-based compounds and to study their nonlinear optical properties in the solid state for the future applications in electronic and photonic molecular devices.

Epitaxial Growth of Lead Phthalocyanine Film on KI Single-Crystal Substrate

Lead phthalocyanine exhibits unique properties among the phthalocyanine family due to its special molecular structure. Those reported so far are apparent one-dimensional metallic conduction in the monoclinic modification thin films, electrical switching effects, and high sensitivity to NO_2 gas. However, these properties depend strongly on the film structures, and structure control such as epitaxy has not been reported in PbPc. To get well-defined thin films for various applications, it is necessary to know the mechanism of epitaxial growth in PbPc. Therefore, in this work, PbPc films were grown on KBr and KI single-crystal substrates at room temperature by the MBE technique with the intention of realizing epitaxial growth. A new type of epitaxial structure with incommensurate matching was derived from SEM and EDP analyses to be KI(001)(5×10/7)R45°-PbPc, which is very different from that found in other phthalocyanines. The epitaxial growth was further confirmed by UV/visible spectral study. Two new types of PbPc crystal structures were proposed based on the derived epitaxy and X-ray diffraction analysis.

Growth of Double-Layer Film (Chloroaluminum Phthalocyanine/Vanadyl Phthalocyanine) by the Molecular Beam Epitaxy

Interest in organic multilayer systems for electric and optical applications has been increasing significantly. Organic crystals are composed of discrete molecules held together by the relatively weak van der Waals forces. Therefore, the potential exists for fabrication of high quality heterostructures or multilayer structures without inducing large strains using a variety of organic crystalline materials. Such structures have potential uses for the study of

excitons in organic crystals, and furthermore, for tailoring the linear and nonlinear optical and electronic properties of organic semiconductors in photonic device applications.

Both AlPcCl and VOPc molecules have pyramidal structures and are particularly appealing for their relatively large third nonlinear optical susceptibility $\chi^{(3)}$. Therefore, their heteroepitaxial growth is expected to exhibit interesting optical and electrical properties. In this work, the epitaxial growth of AlPcCl on VOPc unidirectionally oriented film on KBr substrate was realized using MBE technique at the substrate temperature of 70° C. SEM observation indicated that the AlPcCl layer exhibits unidirectionally oriented epitaxy and is most probably of the unidirectionally oriented tetragonal lattice structure, which resembles the one of the VOPc layers. The epitaxial growth of the AlPcCl layer on VOPc was further confirmed by the low temperature spectral studies at 90 K.

Optical Second- and Third-Harmonic Generations in MBE-Grown Vanadyl Phthalocyanine Thin Films

Phthalocyanines are a two-dimensional π-conjugated system and have been reported to show relatively large $\chi^{(3)}$ values, fast response time, and high photochemical stability. However, up to now, most of the studies were dealing with polycrystalline or amorphous Pc films. In this work, they have extended the nonlinear optical studies to the unidirectionally oriented VOPc epitaxial films in an attempt reach a general understanding of the structure-nonlinearity relationship of two-dimensional π-electron systems. The principal behavior of SHG and THG in unidirectionally oriented epitaxial and polycrystalline films of VOPc was studied at the fundamental of Nd:YAG laser(1.06μm). The anisotropy of THG in the unidirectionally oriented VOPc epitaxial film has been successfully measured and demonstrated to be associated with the symmetry elements of the films. The essential features were explained based on the point groups of 4mm for VOPc/KBr and $C_{\infty v}$ for VOPc/silica. It was found that the unidirectionally oriented phase with 4mm symmetry can be distinguished from the polycrystalline phase based on in-plane polarization dependence THG measurements. The off-diagonal component contributes significantly to the nonlinear optical response, which differs from the one-dimensional π-conjugated systems that have only one dominant diagonal compoment. This is a characterstic feature for the two-dimensional systems. Finally, a molecular accommodation model for VOPc on KBr (001) has been proposed according to the derived 4mm symmetry.

Spectral Dependence of the Anisotropy of $\chi^{(3)}$ of Epitaxially Grown Vanadyl Phthalocyanine Film

The symmetry of the VOPc epitaxial film was proven to be 4mm and the anisotropy

of $\chi^{(3)}$ has been studied at wavelength of 1064nm based on the symmetry elements of the film in the preceding work. It was found that the characteristic feature of the unidirectionally oriented film is the anisotropy of $\chi^{(3)}$ In this work, they extended the anisotropy study of $\chi^{(3)}$ to a wide wavelength region from 1020nm to 1980nm aimed at a general understanding of the nonlinear-optical processes of two-dimensional π-electron systems. The spectral dependence of the anisotropy of $\chi^{(3)}$ of MBE-grown VOPc film has been studied by the technique of third harmonic generation, and an explanation given based on the symmetry elements of the film. It is found that the variation of the anisotropy of $\chi^{(3)}$ is a result of thedispersion of the complex ratio $3\chi_{1122}/\chi_{1111}$. There is a sharp "two-photon resonance" in the spectrim of $\chi^{(3)}$, which is located at 1.88 eV above the ground state. Enhancement of $\chi^{(3)}$ is achieved in the unidirectionally oriented VOPc film by one order of magnitude.

Dependence of Off-Diagonal Components of $\chi^{(3)}$ on Substrate Temperature of Epitaxially Grown Vanadyl Phthalocyanine Films

The nonlinear optical properties of epitaxial films, such as the $\chi^{(3)}$ value and response time, depend strongly on the film's quality (orderliness and continuity). Therefore, it is important to establish the optimum conditions for film growth. The normalized off-diagonal ratio $3\chi_{1122}/\chi_{1111}$ is equal to 1 for isotropic films and larger than 1 for 4mm epitaxial films at wavelength of 1.06 mm, thus the ratio can be taken as a standard measure for the judgment of film quality. In this work, the substrate temperature dependence of the normalized off-diagonal ratio $3\chi_{1122}/\chi_{1111}$ of VOPc epitaxial films was studied because the film structure can be strongly influenced by the substrate temperature. The normalized off-diagonal ratios were determined by circular-polarization third harmonic generation measurement. It is revealed that the unidirectionally oriented film with 4mm symmetry can be distinguished from the polycrystalline film by circular-polarization third harmonic generation measurement, and the quality of the epitaxial film can be quantitatively analyzed by the normalized off-diagonal ratio.

審査結果の要旨

有機薄膜の非線形光学効果は現在活発に研究されているが、熱的な安定性を持つことから金属フタロシアニンも有力な有機材料の一つと考えられている。本論文ではアルカリハライド単結晶を基板に用いて種々のエピタキシャル膜を作成し、特にバナジルフタロシアニンについて２次および３次の非線形光学感受率の角度依存性と波長依存性の測定を行って、新しい現象を見出している。

まずＭＢＥの技法を用いて沃化カリウム上に鉛フタロシアニンの配向膜を作成し、その構造を電子顕微鏡、電子線回折、Ｘ線回折、電子スペクトルによって推定している。この構造は他の金属フタロシアニン配向膜で知られている構造とも、また単斜晶系型や三斜晶系型の単結晶の構造とも異なっている事を見出した。

次に塩化アルミニウムフタロシアニン配向膜は臭化カリウム上で二つの方向を持つドメイン構造を形成するのであるが、バナジルフタロシアニンは単一ドメイン構造である。このバナジルフタロシアニンに塩化アルミニウムフタロシアニンを堆積することによって、単一ドメインの配向膜を作成するのに成功した。またこの手法を用いると有機超格子構造も作成できることを示した。

バナジルフタロシアニンの配向膜を用いて２次および３次の高調波偏光強度の角度依存性を観測してこの膜における構造の対称性を４mmと決定した。そしてこの対称性から期待される結晶構造を推定している。

次に３次の非線形感受率$\chi^{(3)}(3\omega)$の絶対値の測定を行った。配向膜の絶対値は無配向膜の値に比べて約一桁大きい。また入射光の波長を 1000-1900nmの間で掃引し、$\chi^{(3)}$のスペクトルを測定している。このスペクトルの測定はフタロシアニンの膜では初めてであり、他の物質でもまだ少ないので、高く評価される。２光子吸収に相当すると思われる共鳴効果が現れており、またこれが４mmの対称性を持つ膜に特有のものであるとの予備的な結果も得られており、今後の発展が期待される。

また、この対称性を持つエピタキシャル膜では３次の非線形感受率の非対角項χ_{1221}が非常に大きいために、膜の品質を定量的に評価するのに円偏光を用いた３次の高調波によるχ_{1221}の観測が有効であることを提案している。

試験は５０分間の論文発表に続く約１００分の質問時間で、分光学、対称性、非線形光学の基礎的な知識についての質問を行った。この結果、房君は薄膜作成の実験技術を修得し、フタロシアニンの化学、非線形光学の分野の研究の背景を理解していると判断した。また論文を平易な英文でまとめており、英語に関する学力については問題ないと判断した。

以上、房君は論文を中心としてその周辺分野まで含めて幅広い学識を有していると判断した。

また、公開発表会において研究発表とそれに対する質疑応答が行われ、最終的に合格と判定した。